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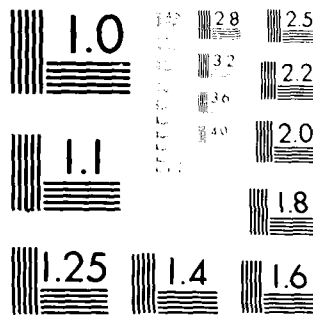
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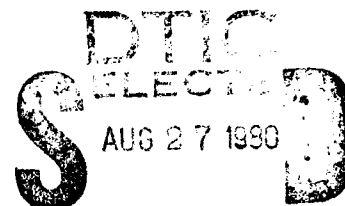
PHENOLIC WASTEWATER TREATMENT ALTERNATIVES

ROBERT G. BLUM
ENVIRONMENTAL SCIENCES BRANCH

JUNE 1980

FINAL REPORT

AUGUST 1979 — FEBRUARY 1980



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(RCRA) will impact upon certain treatment and disposal practices. Therefore, the principal objective of this study is to determine the most cost-effective process(es) for the treatment and disposal of these wastes in accordance with existing and proposed environmental regulations.

A literature review is conducted which examines the following systems/processes: Granular Activated Carbon (GAC) adsorption, ozone oxidation, hydrogen peroxide oxidation, potassium permanganate oxidation, iron (VI) ferrate oxidation, catalytic oxidation, chlorine oxidation, chlorine dioxide oxidation, aeration, recovery, incineration, pyrolysis, landfilling, activated sludge, trickling filter and source control. The results of the cost analyses show that biological processes are by far the most cost-effective alternative for the treatment of paint stripping wastewater at the source. Biological systems are also the most cost-effective for treatment of phenolic wastewater at the industrial or sanitary wastewater treatment plant, closely followed by ozone oxidation. The most cost-effective method for treatment of the highly concentrated phenolic waste is presently in a chemical waste landfill. However, due to stringent regulations being imposed upon such landfills as a result of the RCRA, this method will either become a lot more costly or banned entirely. If the future economics or legality of the situation dictate, incineration of these wastes would be the next best alternative. The economics of a phenol recovery system make it unfavorable at this time.

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PREFACE

This study was performed under program element 62601F, project 1900, task area 70, work unit 11. The author and principal investigator was 1st Lieutenant Robert G. Blum of the Environmental Sciences Branch of the Air Force Engineering and Services Center located at Tyndall AFB, Florida 32403.

This report has been reviewed by the Public Affairs Office (PA) and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

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SECTION I

INTRODUCTION

The treatment and disposal of phenolic wastewaters have been a major environmental concern to the military as well as private industries. The detrimental environmental effects of this pollutant are widely recognized and well documented. Phenols are toxic to most organisms; impart objectionable tastes and odors to drinking water; taint fish flesh at concentrations far below the toxic level; and can deplete the oxygen in a receiving body of water. Phenols are toxic to fish at levels as low as 0.1 milligrams per liter (mg/l) (Reference 1). When phenols combine with chlorine in water, chlorophenol is formed which is even more toxic than phenol. Furthermore, as little as 5 micrograms per liter (ug/l) of chlorophenol in a water supply will cause taste and odor problems (Reference 2).

Phenolic compounds include a wide variety of organic chemicals which may be classified as either monohydric, dihydric or polyhydric phenols, depending upon the number of hydroxyl groups attached to the aromatic ring. Examples are phenol itself (benzophenol), the cresols, xylenols, resorcinols and naphthols. They are solid or liquid at room temperature with relatively high boiling points.

The U.S. Air Force uses phenol-based compounds primarily in aircraft paint stripping operations and, to a lesser extent, in the removal of carbon or paint from various components. The paint stripping procedure involves brushing or spraying the viscous paint remover on the aircraft surface. This stripper is allowed to remain on the surface for a period of time, while it wrinkles and softens the old paint. The loosened paint is then washed free from the surface with a high pressure stream of water. Depending upon the component being stripped, this procedure may be repeated several times. The final step is to wash

the section with detergent then rinse with clean water. The aircraft is then repainted in order to prevent metallic corrosion. In addition, various aircraft and machine components are depainted in vats of highly concentrated phenol. These vats are periodically dumped and refilled with new stripper when the old stripper starts to lose its effectiveness. These two different operations thus constitute the primary source of Air Force phenolic wastes. These processes are accomplished at "Corrosion Control Facilities" located at numerous installations, but the Air Logistics Centers (ALCs) are the largest users of phenolic compounds.

The majority of the wastewaters generated by these phenol-using operations are discharged directly to a sanitary or industrial wastewater treatment plant. In some cases, the introduction of phenols to a wastewater treatment plant using biological treatment processes (e.g., activated sludge, aerated lagoon, and trickling filter) could reduce its efficiency. In other cases, the treatment process simply does not reduce the effluent phenol concentration to an acceptable level. Both of these situations could result in a treatment plant violating its National Pollution Discharge Elimination System (NPDES) permit under the Clean Water Act of 1972. There are also a few bases which are disposing of the highly concentrated phenol wastes in landfills and surface impoundments. Upon final promulgation of the Resource Conservation and Recovery Act (RCRA) (expected in April 1980) these disposal methods may become unlawful. Thus, a need exists for evaluating the various technologies for treating phenolic wastewater from the standpoint of efficiency, economy, and legality of the treatment/disposal process.

There are many systems presently available which effectively treat phenolic wastewaters. However, there is no guidance available to the Air Force regarding selection of these systems in the design and construction of treatment works. Such guidance is necessary since most architectural and engineering (A&E) firms

simply propose and design a "familiar" treatment system without conducting an economic analysis of the alternatives.

The objectives of this study are, therefore:

1. To conduct a literature review of current treatment technologies for phenolic wastewater.
2. Perform an engineering and cost analysis of these treatment systems.
3. Recommend (based on the analyses in Item 2), the most cost-effective process(es) to satisfy USAF requirements.

This report will thus be of value to the Air Force by reducing A&E firm design cost and ensuring the Air Force gets the most effective and economical phenol treatment/disposal system to do the job, while remaining in compliance with federal laws.

SECTION II

REVIEW OF PHENOLIC WASTEWATER TREATMENT TECHNIQUES

1. ADSORPTION - GRANULAR ACTIVATED CARBON

Several methods for phenol adsorption have been reported in the literature, the most notable being the use of granular activated carbon (GAC). (The use of powdered activated carbon is not considered due to problems associated with its recovery and regeneration.) Polymers and ion exchange resins are also considered to be adsorbents; however, these processes will be examined in the section on "Recovery Systems" to which they are more applicable.

Activated carbon is generally used as a polishing step for wastewater subsequent to biological or chemical treatment. However, many industrial wastewaters contain toxic organics which are not amenable to biological treatment or are not effectively removed by chemical treatment. In these cases, treatment by activated carbon may be preferable. GAC has been used effectively in treating wastes from petroleum refineries, coke operations in steel mills, wood preserving, and aircraft paint stripping operations, yielding phenol effluent concentrations of 1 mg/l or less (Reference 3). The phenol is removed from the GAC either by chemical regeneration, which permits recovery of a concentrated phenolic stream, or by thermal regeneration which destroys the phenol. Another potential regeneration process (still in the research phase) is biological, in which bacteria utilize the adsorbed phenol as a substrate thereby removing it from the carbon.

A pilot plant study by Perrotti (Reference 4) using GAC columns showed that the concentration of other constituents in

the wastewater has a considerable effect on phenol adsorption. He recommended solids removal by filtration prior to phenol treatment with GAC. Perrotti also determined that Nuchar WV-W had the highest efficiency for phenol removal of the 12 carbons he tested. Perrotti's experiments were performed on paint stripping wastewater from Kelly AFB (Texas), the profile analysis of which appears in Table 1.

He reported the following additional findings:

- A minimum contact time of 30 minutes must be used in any activated carbon system to properly treat the phenolic paint stripping wastewater.
- At 10 percent average leakage (based on an average of 920 mg/l phenol), the average removal capacity for four runs at 30 minutes residence time was 0.052 gram phenol/gram carbon.
- Thermal regeneration of the carbon appeared to be generally effective in restoring the adsorptive activity of the carbon.
- Although the activated carbon did reduce the level of total chromium in the wastewater, the adsorbed chromium did not affect the thermal regenerability of the carbon.
- On-site thermal regeneration would be more economical than custom regeneration for the amounts of carbon needed to treat the entire wastewater flow (10 gallon per minute (gpm)).
- Activated carbon pretreatment of the paint stripping wastewater will reduce the phenol concentration to an acceptable level.

TABLE 1. PROFILE ANALYSIS OF PHENOLIC TYPE
PAINT STRIPPING WASTEWATER IN
PERROTTI'S STUDY

<u>Parameter</u>	<u>Concentration Range</u>
Phenol	1,040 - 4,060 mg/l
pH	8.0 - 8.6
Total Phosphate (as P)	10.0 - 28.0 mg/l
Suspended Solids	107 - 303 mg/l
Volatile Solids	458 - 2,700 mg/l
Total Solids	800 - 3,830 mg/l
COD	9,200 - 36,400 mg/l
COD Filtered (0.45 microns)	7,250 - 35,100 mg/l
Total Chromium	17.5 - 59.5 mg/l
TOC	2,710 - 14,400 mg/l
TOC Filtered (0.45 microns)	2,520 - 13,600 mg/l
Methylene Chloride	75 - 2,000 mg/l
Surfactants	120 - 4,000 mg/l
Oil and Grease	8.40 - 66.3 mg/l

Zigorski (Reference 5) reported the following conclusions (relevant to this report) from experiments conducted on the removal of 2,4-dichlorophenol and 2,4-dinitrophenol from polluted wastes:

- The adsorption of phenolic compounds by GAC was extremely rapid. Approximately 20 to 30 seconds of contact was required for complete removal of a pure 2,4-dichlorophenol solution with a column of adsorbent operating under optimum conditions.

- Maximum adsorption of phenols occurred at a pH value about 0 to 2 units less than the pKa (acidity constant) value of the phenol.

- Adsorption of phenolic compounds was decreased as the temperature of the system was increased.

- The mesh size of the GAC had no influence on the amount of 2,4-dichlorophenol and 2,4-dinitrophenol adsorbed at equilibrium. However, the rate of adsorption of phenolic compounds increased with decreased mesh size.

- The total adsorptive capacity of the GAC was greater in a solution containing a mixture of phenols than in a solution containing only one phenol.

- Variation in the linear velocity of the solution through a carbon filter between 0.4 and 2.2 feet/minute (2 to 9.7 gpm/ft²) had no significant influence on the amount of phenols adsorbed.

- Of the nine carbons evaluated, Columbia LCK activated carbon was found to be superior.

A pilot plant study by Short, et al., (Reference 6) on removing phenols from refinery wastewaters employed GAC columns following dual-media filtration to reduce the suspended solids and oil content to an acceptable level. According to the authors, this was a necessity in the handling of refinery wastewater with activated carbon since excess solids or oil plugged the column prematurely. During the pilot test, an influent containing 3.38 mg/l phenol was circulated to: (a) an activated sludge unit followed by a GAC column, and (b) GAC treatment alone. The activated sludge effluent contained a median 0.013 mg/l phenol for a 99.6 percent removal. This effluent concentration was then lowered to 0.001 mg/l (99.97 percent removal) following GAC treatment. The activated carbon system (acting alone) reduced the effluent concentration to 0.003 mg/l for a 99.91 percent removal. From these results, activated carbon appears to be much more effective in treating phenols than activated sludge alone.

Henshaw (Reference 7) of Rhodia, Inc., (a manufacturer of herbicide) reported that the company selected a GAC treatment system for its phenolic wastewaters because in cost and performance it out-performed several processing alternatives, including conventional biological systems, chlorination, ion exchange, and oxidation using ozone, peroxide or permanganate. He also stated that the GAC treatment offers a few important side benefits for the herbicide plant: alcohol and phenoxyacetic acid are completely removed from the effluent, suspended solids are filtered out, and the carbon adsorbs dissolved organic compounds that are not responsive to clarification techniques or to biological degradation. The total capital cost (1970) for the plant which treats 150,000 gallons/day (gpd) was \$300,000. This cost is broken down to \$230,000 for the adsorption and reactivation systems, \$40,000 for neutralization, and \$30,000 for process water collection equipment. Direct annual operating costs of the plant, including labor, utilities, and makeup carbon are \$19,500. This yields an operating cost of 35.6 cents per 1,000 gallons of treated water.

Shumaker (Reference 8) reported that the Reichhold Chemical Company (Tuscaloosa, Alabama) chose a physical-chemical plant which included GAC treatment of their phenolic wastewater. The company established that its treatment plant loading was as follows:

BOD = 16,444 pounds per day (lb/day) (3900 parts per million (ppm))

COD = 26,718 lb/day (6400 ppm)

Phenols = 1,540 lb/day (370 ppm)

pH (average) = 9.8

pH (range) = 5.4 - 12.3

The volume of effluent treated was 500,000 gpd and each adsorber contained 124,000 pounds of granular activated carbon. At the design flow of 175 gpm per adsorber, the empty bed contact time was 173 minutes. Phenol removal has been in the range of 99.0 to 99.2 percent with annual operating costs at \$320,000 excluding amortization. The author expects that these costs will be reduced to the range of \$230,000 to \$250,000 per year after the plant has operated for a year.

Lanouette (Reference 3) stated in his article, "Treatment of Phenolic Wastes," that it may be necessary to pretreat the waste stream before it is applied to the carbon beds. The suspended solids concentration in the influent to a downflow column should be less than 60 mg/l, and the oil content should be less than 20 mg/l. Lanouette also reported that operating results indicate that the capacity of the carbon varies from 0.09 to 0.4 gram phenol/gram of activated carbon. Carbon may remove other organic materials present in the phenol-containing stream, and therefore, the loading of the activated carbon is a function of the total organic material adsorbed and not only of the phenol present in the waste stream. The author observed that actual field experience indicated that carbon capacities are substantially greater than calculated from isotherms, possibly as a result of biological activity in the carbon columns.

Kroop (Reference 9) conducted a laboratory investigation which assessed the effectiveness of phenol removal from aircraft paint stripping wastewater using: (a) oxidation with ozone, (b) oxidation with potassium permanganate, and (c) adsorption with GAC. He concluded that granular activated carbon adsorption with thermal regeneration was the best treatment process for treating phenolic aircraft paint stripping wastewaters; it provided better reduction of phenols and COD than did either ozonation or potassium permanganate and was less expensive to construct or operate.

2. CHEMICAL OXIDATION PROCESSES

a. Ozone

Ozone is a powerful oxidant which has historically been used for disinfection of municipal water supplies (mainly in Europe). In recent decades, however, ozone has attracted considerable interest for its use in wastewater treatment. Ozone has been found useful in the following areas of water treatment: (1) color removal, (2) taste and odor removal, (3) disinfection, (4) iron and manganese removal, (5) phenol oxidation, and (6) cyanide oxidation. Because ozone is a relatively unstable gas, it is generated on site from air or pure oxygen which is passed between high voltage electrodes. Theoretically, 1058 grams of ozone can be produced per kilowatt-hour (gms/KW-hr) of electrical energy; however, an ozone production of only about 150 gms/KW-hr is realized with most commercial generators as a result of heat losses.

While ozone can oxidize phenol completely to carbon dioxide and water, the usual practice is to oxidize the phenolic waste to intermediate organic compounds that are toxic but readily biodegradable. In order to accomplish this, ozone is required in the range of 1.5 to 2.5 parts of ozone per part of phenol (Reference 3). As the concentration of phenol in the waste decreases, the relative proportion of ozone needed increases. Also, if other oxygen-demanding materials are present in the waste stream then the ozone requirement will be higher to meet this additional demand. Table 2 illustrates the varying values for ozone-phenol ratios extracted from Lanouette's article (Reference 3).

TABLE 2. VARIATION IN OZONE-PHENOL RATIOS

<u>Source</u>		<u>Initial phenols, ppm</u>	<u>Ozone concentration ppm</u>	<u>Ozone/phenol ratio</u>	<u>Residual phenols, ppm</u>
Coke Plant	A	1,240	2,500	2.0	1.2
	B	800	1,200	1.5	0.6
	C	330	1,700	5.2	1.0
	D	140	950	6.8	0.1
	E	127	550	4.3	0.2
	F	102	900	8.8	0.0
	G	51	1,000	20.0	0.4
	H	38	700	18.0	0.1
Chemical Plant		290	400	1.4	0.3
Refinery	A	605	750	1.3	0.3
	B	11,600	11,000	1.0	2.5

Eisenhauer (Reference 10) found that phenol degradation by ozone could be described by the following rate expression:

$$\ln \left(\frac{P_o}{P_t} \right) = \frac{K_1 R t}{F^{1/3}}$$

where:

P_o = initial phenol concentration

P_t = phenol concentration at time t

R = ozone dose rate (mole O_3 /mole phenol/min)

F = ozone flow (l/min)

K_1 = phenol degradation rate constant (mole phenol/mole O_3 /dia) where the dia is the diameter of the ozone gas bubble. The ozone gas bubble diameter has been shown to be numerically equal to the $1/3$ power of the gas flow ($F^{1/3}$).

t = time

Eisenhauer also investigated the effect of pH upon the ozone oxidation of phenol and reported the data shown in Table 3. This table shows that the phenol degradation rate more than doubles at a pH above 11.0. Niegowski (Reference 11) has shown that this rate continues to increase up to a pH of approximately 11.8. Furthermore, it has been indicated that at elevated pHs, ozone becomes more selective for phenols than other organics or oxidizable materials present in the wastewater (Reference 11). Eisenhauer studied the effect of reaction temperature and found that within the range of 20 to 50°C, there was no significant effect of temperature on the rate of phenol ozonization. However, at elevated temperatures a greater portion of the phenols were oxidized completely to CO₂.

TABLE 3. EFFECT OF pH ON OZONE OXIDATION OF PHENOL

Initial pH	Final pH	K ₁
3.00	2.93	0.229
5.01	3.44	0.247
5.57*	3.30	0.256
9.14	3.60	0.307
11.06	9.90	0.658

*Ambient pH, not adjusted initially.

The oxidation of phenols by ozone is given by the chemical equation $C_6H_5OH + 5O_3 \Rightarrow 3H_2O + 6CO_2$ which indicates that 5 moles of ozone are required to oxidize 1 mole of phenol to carbon dioxide and water. However, due to the formation of intermediate products, Eisenhauer found that 14 moles of O₃ are required for the complete oxidation of 1 mole of phenol to CO₂ and H₂O. Gould and Weber (Reference 12) determined that virtually complete removal of phenol and its aromatic degradation products is realized when 4 to 6 moles of ozone have been consumed for each mole of phenol originally present. At this point, however, they found

that approximately one-third of the initial organic carbon will remain, being about evenly divided between glyoxal and glyoxylic acid. Gould and Weber concluded that ozonation to the point of 100-percent removal of organic matter would be exceedingly costly and time consuming. However, if the reaction intermediates create no further treatment/disposal problems, then the study suggests that ozonation will provide a satisfactory degree of treatment for most purposes.

A report by Nebel, et al., (Reference 13) contended that 5 moles of ozone per mole of phenol would not be practical since unnecessarily large quantities of ozone would be consumed. They suggested that a more realistic approach would be to determine the minimum amount of ozone that would destroy the phenol and yield harmless oxidation products that could then be readily biodegraded with further treatment. Their study showed that approximately 2 moles of ozone were required for complete destruction of 1 mole of phenol. (This is equivalent to 1 gram of ozone to destroy 1 gram of phenol, since the molecular weight of phenol is approximately double that of ozone). They also claimed that the ozone oxidation products are nontoxic to microorganisms and higher forms of fish life. However, the test solution used to conduct this bioassay was obtained by ozonizing an initial solution with a phenol content of 200 mg/l down to 0.1 mg/l. This represents a phenol removal of 99.95 percent, and it is not clear what the intermediate oxidation products were at this point. Furthermore, the article did not say what quantity of ozone was required to reduce the phenol concentration of the test solution. The operations of several manufacturers using ozone to treat their phenolic effluents were also described in the article. Pretreatment was required in most cases to remove high ozone-demanding constituents (other than phenol) and to adjust pH.

According to Fox and Himmelstein (Reference 14), the ozone treatment of phenols does not reduce the TOC content of the waste, hence this method should not be used if reductions in organic discharges are required. This was corroborated by Niegowski (Reference 11) who showed that a 99 percent reduction of phenols produced only a 50 percent reduction in chemical oxygen demand.

McKinney (Reference 15) concluded that activated sludge microorganisms acclimated to phenols had significant difficulty in metabolizing the intermediate aromatic compounds of catechol and hydroquinone.

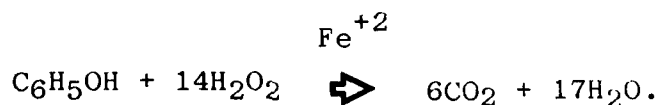
A cursory cost analysis by Throop and Boyle (Reference 16) determined that for flows in excess of several million gallons per day (mgd), ozonation appeared to be the least costly method. The analysis pertained to three sources of wastewater at a major foundry with flows of 1.3 mgd, 2.4 mgd, and 2.9 mgd, respectively; and phenol concentrations ranging from 0.110 to 0.123 mg/l. Phenol reduction down to 0.001 mg/l or below was desired, and this required an ozone to phenol ratio of about 50:1 by weight. The alternative unit processes investigated were chlorination, potassium permanganate, hydrogen peroxide, and carbon adsorption. It should be noted that these were unique phenolic wastes with very low phenol concentrations; thus, this analysis would not necessarily be applicable to other phenol wastewater.

Kroop (Reference 9) studied the ozone oxidation of phenol (paint stripping wastewater) in batch experiments and observed that phenol reductions of 99.7 percent yielded COD reductions of only 57 percent. The formation of CO_2 was not substantial, suggesting the formation of intermediate oxidation products. In continuous flow experiments, the highest obtainable COD reduction was 65 percent, leaving 3500 mg/l of COD in the wastewater. To satisfy the arbitrary ozone demand of 99 percent phenol reduction, 5.2 moles ozone/mole phenol was required, or a weight ratio of 2.7.

b. Hydrogen Peroxide

The value of hydrogen peroxide in wastewater is based on its ability to oxidize a number of toxic and noxious substances. It will react with sulfide, mercaptans and amines, as well as with phenols. Specific applications of H_2O_2 have included: (a) effluent polishing to remove the final traces of phenol from a biological treatment system effluent; (b) batch treatment for high-level phenolic wastes; and (c) an emergency back-up to other treatment systems. In addition, Kibbel (Reference 17) reported that hydrogen peroxide is an excellent source of dissolved oxygen, which enhances the activity of aerobic organisms in wastes.

The stoichiometric equation for the reaction of hydrogen peroxide with phenol is:



The presence of metal salts, particularly iron salts, as a catalyst is necessary for the completion of the oxidation reactions.

The FMC Chemical Corporation (Reference 18) investigated the effect of various catalysts including ferrous sulfate, iron wool, nickel salts, aluminum salts, and enzymes over a temperature range of 70 to 120°F. Table 4 shows the effect of temperature according to data provided by the FMC Corporation. Although there is not sufficient data to draw a reliable conclusion, a report by the FMC Corporation stated that the reaction was independent of temperature. Table 5 shows the effect of catalyst and H_2O_2 /phenol ratio abstracted from reference 18. According to the FMC report, neither increasing the iron level to 0.03 percent nor adding aluminum salts affected the overall phenol oxidation, total oxidizable carbon, or chemical oxygen demand. (Again, however, there seems to be insufficient data to draw this

conclusion.) Metallic iron, as demonstrated by the use of steel wool, appeared to be an effective catalyst, and nickel chloride was almost totally ineffective.

TABLE 4. EFFECT OF TEMPERATURE ON THE HYDROGEN PEROXIDE
OXIDATION OF PURE PHENOL

Catalyst Concentration (Percent Fe)	Temperature(°F)	Phenol(mg/l)	TOC(mg/l)	COD (mg/l) (theoretical= 1190)
None		500	383	1,105
0.01	70	3.4	375	561
0.01	90	5.0	365	710
0.01	120	9.0	380	760
0.03	70	2.1	370	729
0.03	90	1.7	355	760
0.03	120	22.0	357	620

Initial Concentration = 500 mg/l, 1.0 H₂O₂/1.0 phenol weight ratio, 30-min retention time, initial pH = 5.5, Fe added as ferrous sulfate.

TABLE 5. EFFECT OF CATALYST AND H₂O₂/PHENOL RATIO
ON THE OXIDATION OF PURE PHENOL

H ₂ O ₂ :Phenol				
Ratio	Catalyst	Phenol(mg/l)	TOC(mg/l)	COD(mg/l)
None	None	500.0	383	1,105
0.5	None	499.0	365	
1.0	None	493.0	375	
0.5	0.01%Fe	88.0	380	974
1.0	0.01%Fe	7.0	360	679
2.0	0.01%Fe	0.3	310	392
3.0	0.01%Fe	0.2	150	106
4.0	0.01%Fe	0.003	138	66
0.5	0.03%Fe	118.0	365	1,020
1.0	0.03%Fe	22.0	345	620
2.0	0.03%Fe	0.2	315	418
3.0	0.03%Fe	4.04	210	150
0.5	0.01%Fe, 0.01%Al	79.0	380	971
1.0	0.01%Fe, 0.01%Al	4.0	310	625
2.0	0.01%Fe, 0.01%Al	0.1	300	495
3.0	0.01%Fe, 0.01%Al	0.05	200	172
4.0	0.01%Fe, 0.01%Al	0.006	196	105
1.0	0.03%Fe, 0.03%Al	5.7	310	510
2.0	0.03%Fe, 0.03%Al	0.3	320	405
3.0	0.03%Fe, 0.03%Al	0.2	225	210
1.0	Steel Wool	16.0		
	(Room temp., 10- min retention)			
0.5	0.01%Ni (as NiCl ₂ 6H ₂ O) (Room temp. test)	496.0	370	

Initial phenol concentration = 500 mg/l; 120°F; 30-min retention time; initial pH = 5.5; Fe added as ferrous sulfate; Al added as aluminum sulfate.

The FMC Corporation recognized that the optimum pH for the H_2O_2 oxidation of phenol had been reported in the literature (Reference 19) as 3-4 pH units. They explained that although their experiments were started at a pH of 5-6, it rapidly dropped to the 3-4 level during the reaction.

Experiments by Keating, et al., (Reference 20) revealed that the reaction between hydrogen peroxide and phenol is essentially completed in 30 minutes when iron catalyst is present at 5 mg/l using 50 mg/l of phenol and a 3:1 weight ratio (8:1 mole ratio) of hydrogen peroxide to phenol. They recommend an iron:phenol weight ratio of from 0.5-1.0:100 when phenolics are no greater than 2000 mg/l; and at least 1.0:100 for higher phenol concentrations. For treatment of phenolic mixtures (i.e., substituted phenols), they recommended at least a 3:1 weight ratio of peroxide to total phenol, with additional amounts if large quantities of fast reacting phenolic species (e.g., certain substituted phenols such as 2,4-dimethylphenol and 2,4-dichlorophenol) are present. This ensures adequate peroxide available to the slower reacting compounds to reduce them to the desired low levels in a specified time period.

A study by Burbank, et al., (Reference 21) using refinery wastewater showed that phenol removal is directly related to the amount of hydrogen peroxide to phenol ratio; whereas removal of COD is virtually independent of this ratio. The authors stated that this is due to the formation of unoxidizable compounds with the breakdown of phenol. (In this sense, phenol removal is not necessarily translated into COD removal.) The end products of total phenol destruction were short-chained acids and aldehydes which were resistant to further chemical oxidation by hydrogen peroxide, exerted COD, and were easily removed by biological treatment. In the experiments conducted, an H_2O_2 :phenol weight ratio of 3:1 yielded only a 60-percent phenol removal after 40 minutes retention time; a ratio of 20:1 yielded virtually

100-percent removal after 30 minutes; and a 30:1 ratio resulted in virtually 100-percent phenol removal after 15 minutes contact time. The characteristics of the refinery wastewater used in this study are shown in Table 6. Note that the average phenol concentration of this wastewater was only 7.2 mg/l.

TABLE 6. CHARACTERISTICS OF REFINERY WASTE TREATED BY THE API SEPARATOR

Characteristic	Concentration		
	Average	Minimum	Maximum
Oil and Grease, mg/l	10	1.3	110
Suspended solids, mg/l	10	0	160
Settleable solids, mg/l	0.2	0.1	0.5
Phenol, mg/l	7.2	5.0	10.6
Sulfide, mg/l	0.5	0	3.0
Ammonia, mg/l	16.0	5.0	75.0
COD, mg/l	550	300	3700
BOD, mg/l	*	210	*
pH	8.6	8.4	8.8
Temperature, °F	111	111	112

*Not given in report.

c. Potassium Permanganate

Potassium permanganate is a powerful oxidizing chemical which has been used in both water and wastewater treatment for removal of phenol, manganese, iron, sulfide, algae, cyanides, and radioactive contaminants. The stoichiometric equation for the reaction of permanganate with phenol is given by:



This represents a theoretical weight ratio of 15.7 grams KMnO_4 required to oxidize one gram of phenol. However, Lanouette (Reference 3) reports that weight ratios of 6 to 7 grams KMnO_4 per gram of phenol have been found to be effective. He also states that the reaction seems to proceed favorably in the pH range from 7 to 10, but below pH 7 retention times become excessive.

The manganese dioxide (MnO_2) precipitates as a hydrous sludge which must be removed. This sludge becomes a problem if coagulation, sedimentation and/or filtration operations are not employed. However, if coagulation and sedimentation processes are utilized, the sorptive properties of the hydrous MnO_2 often render it beneficial to clarification (Reference 22). On the other hand, it would increase the quantity of sludge requiring disposal.

In an experiment using actual phenolic aircraft paint stripping wastewater, Kroop (Reference 9) found that potassium permanganate was not an effective oxidizer of phenols and created a sludge problem. The best performance was a phenol concentration reduction from 2800 mg/l to 97.5 mg/l which required a dosage ratio of 25.2 mg KMnO_4 /mg phenol. The characteristics of the wastewater tested by Kroop are given in Table 7.

TABLE 7. CHARACTERISTICS OF SETTLED PHENOLIC AIRCRAFT PAINT STRIPPING WASTEWATER USED DURING INVESTIGATION

<u>Contaminant</u>	<u>Concentration (mg/l except pH)</u>
Phenols	3000
Methylene Chloride	1600
COD	10100
Total Chromium	100
Filterable Solids	75
pH	8.3

Throop and Boyle (Reference 16), conducted a test of foundry wastewater having an initial phenol concentration of 123 mg/l and a flow of 6.6 mgd. Potassium permanganate was added at concentrations of 1, 5 and 10 mg/l. After a contact time of 20 minutes, the waste was analyzed for residual phenols and the results are shown in Table 8.

TABLE 8. PHENOL REMOVAL AS A FUNCTION OF KMnO_4 DOSAGE

<u>KMnO_4 Dosage mg/l</u>	<u>KMnO_4:Phenol Ratio</u>	<u>Phenol Concentration</u>	
		<u>Initial ppb*</u>	<u>Final ppb*</u>
1	8:1	123	103
5	41:1	123	31
10	80:1	123	**

*Parts per billion **Nondetectable

The Carus Chemical Company (Reference 23) reported that an organic paint stripping facility at a southwestern plant produced phenol concentrations up to 10 ppm at the 2.5-mgd industrial wastewater treatment plant (IWTP). After experimenting with introducing KMnO_4 at several points in the IWTP, it was decided to apply the chemical at the buildings where the stripping was actually being done. This option allowed the permanganate to have a 3 to 4-hour contact time with the wastewater prior to reaching the IWTP. The author stated that this enabled all the phenol to be oxidized prior to combining with other process waters at the IWTP. The KMnO_4 dosages ranged from 5 to about 20 ppm or 200 to 400 pounds/day. The insoluble manganese dioxide produced as a result of the oxidation reaction was coagulated out in the treatment plant. The author concluded that the use of KMnO_4 for oxidizing phenolic wastes produced a phenol-free

effluent at the plant. The products of oxidation were carbon dioxide, potassium hydroxide, and manganese dioxide which were readily handled by the existing system.

d. Iron (VI) Ferrate

Ferrate is iron in its +6 oxidation state and has the molecular formula FeO_4^{-2} . This compound is a relatively powerful oxidizing agent through the entire pH range and decomposes in aqueous solution generating hydroxide ion and molecular oxygen. This is a new chemical to the field of wastewater treatment and shows great promise according to Waite and Gilbert (Reference 24). Experiments on the ferrate oxidation of phenol revealed that ferrate to phenol molar ratios of 10 to 1 were necessary for efficient oxidation to occur. It was observed that ionized phenolate species which formed at high pH values are more highly reactive with ferrate, and greater phenol removals are achieved. The authors' data showed that ferrate and most organic substances have a low reactivity above pH 8, and thus, ferrate would be relatively more selective for phenol at high pH.

e. Catalytic Oxidation (Aqueous Phase)

Katzer, et al., (Reference 25) described and evaluated a catalytic oxidation process designed for 99 percent removal of phenol from two wastewater streams. The first was the wastewater stream from a typical catalytic cracking unit used in the petroleum industry with an effluent containing about 700 mg/l of phenolic compounds; the second case involved the treatment of wastewater from a coke plant with concentrations up to 4000 mg/l phenol. The wastewater was assumed to be prefiltered and clear of all suspended solid materials that might cause plugging or erosion problems in the catalytic bed. The process used compressed air or oxygen and a reactor consisting of a cylindrical vessel that is packed with 0.25-inch spherical catalyst pellets of copper oxide on alumina.

According to the authors, the aqueous phase catalytic oxidation of waste streams with high concentrations of organics is much more economical than adsorption techniques because, at high concentrations, catalytic oxidation becomes thermally self-sufficient, whereas adsorption processes require frequent regeneration and much make-up adsorbent. On the other hand, catalytic oxidation seems to be economically unattractive for low concentrations of organics in ambient temperature wastewater streams because of the energy requirement to heat the streams to a temperature giving a reasonable oxidation rate. The authors stated that various technical problems remain to be solved if aqueous phase catalytic oxidation is to be applied commercially. These problems include the possible slow dissolution of the catalytic component and support, possible poisoning of the catalyst by components in particular wastewater streams, possible plugging of the bed by suspended solids, and optimization of the mass transfer characteristics of the three-phase system.

f. Chlorine

Chlorine can combine with phenols to produce chlorophenols which are even more toxic and refractory than phenols. Therefore, chlorination is not considered to be an effective technique for phenol oxidation and will not be further investigated in this report.

g. Chlorine Dioxide

Chlorine dioxide, unlike chlorine, does not produce chlorophenols but attacks the benzene ring of the phenol to form compounds that are odorless and tasteless. Like ozone, the instability of gaseous chlorine dioxide necessitates on-site generation. The ClO_2 can be generated either from chlorine gas or from hypochlorite. In the pH range of 7.0 to 8.0, ClO_2 will oxidize the phenol compound to benzoquinone with a theoretical requirement of 1.5 times the amount of phenol (Reference 3). At

a pH above 10, ClO_2 will oxidize phenol to maleic acid and oxalic acid, with a theoretical requirement about 3.3 times the amount of phenol.

h. Aeration (Non biological)

Field tests have shown that some phenol removal can be obtained by aeration alone, either quiescent or forced (Reference 3). The tests were designed to study the effects of aeration alone and no effort was made to induce biological degradation. (Visual inspection of the waste after aeration did not show any biological growth).

3. RECOVERY SYSTEMS

Phenol recovery systems are widely used for petroleum refinery wastes, coke-oven liquors, and phenol resin plant effluents, where waste phenol concentrations and flows are relatively high. These systems usually employ a liquid solvent-extraction process which normally consists of a multi-stage contactor, phase separator, raffinate stopper (to remove soluble solvent from the wastewater), and an extract still to recover the extracted chemicals.

According to Pollio, et al., (References 26 and 27) solvent extractants are particularly suitable in handling highly concentrated phenolic wastes. They generally show less tendency than solid adsorbents to be sensitive to variations in pH and phenol concentrations of the wastes being treated. Furthermore, the presence of certain foreign solutes usually reduces the efficiency of the overall adsorption process.

Kiezyk and Mackay (Reference 28) stated that for high phenolic concentrations, solvent extraction has been found to be the most economical and efficient treatment method. They reported that developments in extraction have led to more efficient

contacting devices (such as centrifugal and rotating disc contactors) and removal efficiencies of 98.8 and 99.9 percent, respectively, have been achieved.

A process employing extraction and distillation techniques with a proprietary solvent is capable of reducing phenol to less than 1 ppm in the waste stream (Reference 29). Since the process employs liquid-liquid extraction as the first step in the removal and recovery of phenol, it can handle a variety of incoming phenol concentrations, typically ranging from 500 mg/l to 9 percent (saturation). According to the authors, capital and operating costs allow for high return on investment. A study of economics and specifications for a commercial phenol recovery plant with a 25 gpm feed rate shows a 197 percent return on investment. The phenol recovered was 99 percent pure and amounted to a total of 9.35×10^6 pounds per year. An additional benefit was the opportunity to recycle the water from the system, thus establishing an essentially closed loop, zero discharge condition for this part of the resin plant.

R. D. Fox, et al., (Reference 14) described a phenol recovery system at Dow's Midland Division which regenerates the activated carbon by caustic desorption. The phenol is recovered and recycled to the phenol plant as sodium phenate. However, this process is only applicable to organic chemicals whose adsorption on activated carbon is affected by change in pH. Fox, et al., proposed the use of an activated carbon, solvent regeneration system for the desorption of a wide variety of organic chemicals. They conducted an economic analysis of recovery versus destruction methods for treating phenol wastes and concluded that, with increased chemical value and fuel costs, recovery processes are becoming more competitive with destructive methods (i.e., biological/chemical oxidation, incineration, and GAC thermal regeneration). However, the phenol waste used in the comparison was assumed to be solids-free with a neutral pH.

Experiments conducted by Jorgensen (Reference 30) showed that phenol can be effectively removed from wastewater by either adsorption on activated carbon, or ion exchange on a strong base anion exchanger. The phenol was recovered by a counter-current elution using a warm (45°C) 1-Molar sodium hydroxide solution.

C. R. Fox (Reference 31) reported that three recovery units are in operation removing phenol from wastewater. One unit recovers phenol from a 1.5 to 2 percent waste stream and has been in operation for more than 6 years using the original resin charge. The resin is regenerated with methanol and the spent regenerant is returned directly to the process. Two units employ acetone as a regenerant; one of them has been operating for more than 3 years removing and recovering phenol from a 0.75 to 1.5 percent aqueous waste stream. This recovery process is cyclic and consists of adsorption, regeneration with acetone, a water rinse, and distillation.

Experiments by Pollio and Kunin (Reference 27) indicated that weak base anion exchange resins, such as Amberlite® IR-45, offer a practical means for treating phenolic waste streams commonly encountered at industries. Though strong base ion exchange resins operating in the hydroxide cycle showed appreciable capacities for phenol, weak base anion exchangers are preferred because they are more stable in the basic form and can be regenerated more efficiently. Furthermore, the authors stated that the capacities of weak base resins for phenol are less affected by the presence of neutral salts in the streams.

Crook, et al., (Reference 32) performed experiments in which industrial waste effluents containing 280 to 6700 ppm of phenol were passed through columns containing Amberlite® XAD polymeric adsorbents. Using Amberlite® XAD-4 a total of 87 grams of phenol per liter of resin could be removed from a waste effluent containing 6700 ppm of phenol with the resultant effluent from the

resin containing less than 1 ppm of phenol leakage. Solvent regeneration of the resin could be accomplished using either acetone or methanol. Acetone (for recycle in the regeneration step) and phenol of 99 percent purity could be recovered by distillation.

4. THERMAL PROCESSES

There are two types of thermal processes which have been reported in the literature: incineration and pyrolysis. Incineration refers to the controlled oxidation of waste to produce the products of complete combustion, primarily carbon dioxide and water. Pyrolysis involves the break up of stable organic molecules to form smaller organic molecules. The breakdown of a stable organic molecule is a function of the temperature and time the waste spends in the system. Some molecules have a particular chemical bond that is far weaker than other bonds. The breaking of this bond may render the organic nonhazardous or even a valuable chemical. In such a situation, by choosing the correct temperature, selective pyrolysis will occur to give the desired products.

There are many types of thermal systems that may be used to treat a variety of wastes. The most notable are the rotary kiln, multiple hearth furnace, fluidized bed incinerator, and pyrolysis systems. In the basic incinerator the feed and air are brought together at elevated temperature and oxidation occurs. To assure complete combustion and provide the temperature, time, and oxygen required to meet standards, an afterburner section is required. Air pollution control equipment is used prior to releasing any products of combustion to the atmosphere. Thermal processes should not be used to treat wastes containing heavy metals.

Pyrolysis systems have not received the attention of incinerators even though they have two main advantages: the volume of gas leaving the unit is about 1/8 that of the incinerator; and this gas may have sufficient energy to be used as a fuel elsewhere in the plant.

Concentrated phenol wastes can be treated by incinerating them for complete destruction to carbon dioxide and water according to the following reaction:



The theoretical heat of combustion for phenol is 13,300 BTU per pound and this heating potential can be utilized in the thermal process. The more concentrated the phenol (or other organics) in the waste, the less auxiliary fuel is required to sustain combustion.

One liquid-phenol incinerator has been in operation for 3 years, burning a phenol-water mixture averaging about 13.5 percent phenol (Reference 3). Atomizing steam is supplied at 125 psi and supplemental fuel oil is added as needed to maintain a combustion temperature at 1600°F (871°C).

Ackerman, et al., (Reference 33) test-incinerated an aqueous phenol sludge and achieved a destruction efficiency of more than 99.999 percent, as indicated by the analysis of combustion gas samples. No organics could be detected in the scrubber water or ash, and stack emissions were analyzed for particulate loading and composition.

A study by Combustion Power Company (Reference 34) showed that selected USAF liquid wastes could be treated in a fluidized bed incineration system. The wastes treated were herbicide orange, petroleum, oil and lubricant wastes (POL), paint stripping wastes, aircraft washrack wastes, municipal garbage and

sewage sludge. Results showed that with proper liquid waste injection, POL wastes or shredded municipal garbage can be used as fuel to dispose of the above liquid wastes.

The incineration of hazardous wastes will be governed by strict standards to be promulgated pursuant to the RCRA. These standards will undoubtedly make incineration more expensive than it is today.

5. LANDFILL DISPOSAL

This alternative also includes disposal in a landfarm, basin or surface impoundment. The fate of phenol in soil environments is difficult to predict at present. There is little information in the scientific literature concerning the behavior of phenol in soils, its possible reactions, and its attenuation by soil components.

Under the Environmental Protection Agency's (EPA's) proposed rules for implementing the RCRA, no waste which is ignitable, reactive, or volatile may be disposed of in this manner. EPA has, in fact, classified paint stripping wastes as ignitable, and phenol wastes in general are considered hazardous. It is therefore possible that regulatory approval will not be given for disposal of USAF phenolic wastes in a landfill, even a permitted hazardous waste landfill. Thus, landfill disposal may no longer be a viable alternative. However, in the event that regulatory approval is given for landfill disposal of these wastes, this method will be considered in the cost analyses of the next section.

6. BIOLOGICAL PROCESSES

The literature is replete with references on the biological treatment of phenolic wastewaters. The main treatment technique reported is activated sludge, with a few articles on rotating biological contactors, aerated lagoons, and trickling filters.

Effective biological treatment of phenolic wastes has been reported over a wide range of phenol concentration, from as low as 7 to 10 mg/l to as high as several thousand mg/l (Reference 3). The phenol serves as an energy source as well as a source of carbon for synthesis of cell mass. End products of the aerobic reaction are carbon dioxide, water, and biological cells. The organisms which can oxidize phenol are abundant in nature and can be found in natural waters and in the soil. These organisms will develop in the wastewater provided that the necessary nutrients for growth are present and environmental conditions are favorable.

In the biological treatment of wastewaters, it is necessary to ensure that pH, nutrient levels, temperature and applied BOD are appropriate to the particular waste treated. The bacteria which oxidize phenol will thrive between pH values of 7 to 9. The nutrients, nitrogen and phosphorus, may be required to provide a phenol: nitrogen: phosphorus ratio of about 70:7:1 (References 35 and 36). Optimum operating temperature has been found to be 30 to 37°C. Food to microorganism (F/M) ratios (pound of BOD applied per pound mixed-liquor volatile suspended solids, per day) should be in the range of 0.2 to 0.3 for optimum operation (References 37 and 38).

The control of shock loads to the biological processes is probably the most critical factor to the successful oxidation of phenol. Numerous studies have shown that phenol concentrations in excess of 500 mg/l can result in significant decreases in

efficiency. One way to solve this problem and ensure process stability is to design completely mixed suspended growth systems using activated sludge or aerated lagoons with relatively long hydraulic detention times. Fixed film systems such as trickling filters are less likely to effectively absorb shock loads unless designed in series or with an equalization basin ahead of the filters.

Since biological treatment systems for phenol are generally aerobic, oxygen is supplied by diffused or mechanical aeration. Approximately 2.5 grams of oxygen are required per gram of phenol at 30°C. Although activated sludge systems offer better control of the process and smaller land requirements, they do represent a higher capital investment and more sophisticated operation than the low solids aerated lagoon. The major operational cost in either case is in supplying oxygen.

Reid, et al., (Reference 39) found from laboratory and pilot studies that phenols can be treated successfully by biological slimes in concentrations as high as 7500 mg/l. The authors stated that a rotating drum works best for very high concentrations of phenol. Their pilot plant studies showed that trickling filters will operate on a sewage and phenol mixture if the phenol concentration is kept below 100 mg/l, and that activated sludge treatment was very successful for phenol concentrations up to 500 mg/l.

Steck (Reference 40) reported that activated sludge is the predominant biological process used in the treatment of phenolic refining wastes in Germany. He stated that with an influent phenol content of 40 to 50 mg/l, an effluent concentration of 0.5 mg/l or less could be expected from a well operated activated sludge unit.

Adams (Reference 41) reported on a project which evaluated the potential of biological treatment for a weak ammonia liquor from a coke plant, which had been pretreated by multi-stage flash evaporation. The wastewater had an average phenol concentration of 3270 mg/l, BOD of 6370 mg/l, and COD of 8230 mg/l. Adams concluded that high concentrations of phenol (on the order of several thousand mg/l) can be reduced to effluent concentrations of less than 0.5 mg/l with the activated sludge process under fairly constant loading conditions. Thus, adequate equalization may be required prior to the activated sludge plant. He found that the degradation of phenols generated a considerable quantity of degradable by-products which may contribute substantial concentrations of soluble BOD to the final effluent. Consequently, the phenol may be reduced to levels less than 0.1 mg/l, but soluble BOD levels as high as 15-30 mg/l may still be present. Adams observed that the treatment of phenolic materials may generate filamentous sludges, particularly in the absence of sufficient trace nutrients. He noted that even under a very carefully controlled operation, the effluent concentration of phenols can only be expected to be less than 0.1 mg/l for 40 percent of the time at organic loadings in the range of 0.2 to 0.3 pound BOD/day/pound mixed liquor volatile suspended solids (MLVSS).

A pilot plant study by Cobb, et al., (Reference 42) showed that the Air Force paint stripping wastewater could be efficiently handled by a biodegradative process. A batch-operated trickling filter utilizing forced aeration and plastic bio-ring support media was able to reduce phenol concentrations from up to 1000 mg/l to less than 1 mg/l. They observed that combined starvation and dehydration interludes supplying no inputs of any kind for more than 6 weeks were survived with rapid (72-hour) recovery to normal performance levels with neither special treatment nor reseedling. Routine 12-hour and 72-hour overnight and weekend "down" periods were tolerated with no alteration in base rates. The advantages of this system are that the growth media is not

seriously affected by shock loading or down periods, and that the paint stripping wastewater could be continually recycled over the media until the desired effluent quality is attained.

Short, et al., (Reference 6) analyzed the phenol treatment efficiencies of four large oil refinery activated sludge plants. Influent phenol concentrations ranged from 0.61 to 11.0 mg/l and effluent concentrations ranged from 0.01 to 0.035 mg/l. They stated that although biological treatment systems showed high capacity for phenol removal, the systems appear to "upset" easily with changes in phenolic levels and, at times, will upset with no apparent cause.

A full-scale activated sludge plant having a design load of more than 4000 pounds of phenol/day has been in operation at a Bethlehem Steel Corporation coke oven plant since 1962. Kostenbader and Flecksteiner (Reference 35) reported that the effluent from this system (which treats the weak ammonia liquor) contains less than 0.1 mg/l phenol, which represents an oxidation efficiency greater than 99.9 percent.

7. SOURCE CONTROL

Although source control does not constitute a treatment technique per se, it can, no doubt, aid in phenolic pollution abatement. Elimination of phenol from the various stripping compounds has been addressed; however, there is not an effective non-phenolic stripper for use on current polyurethane/epoxy paint systems. The Air Force Materials Laboratory (Reference 43) has been trying to develop water-based polymeric coatings which might not require phenolic strippers for removal. However, they have not yet been successful.

Short of elimination of or reduction in the phenolic content of the stripper, other measures can be taken to effect pollution abatement. Schmitt and Zeff (Reference 44) investigated pollution control measures at the Alameda Naval Air Station paint stripping facility. They roughly estimated that a 50-percent reduction in phenol and methylene chloride from the wastewater could be achieved by removal of concentrated paint stripping wastes from the hangar floor prior to water wash-down of the aircraft surface. Other possible measures include the removal of stripper and old paint from aircraft with squeegees or industrial vacuum cleaners, and the filtration of paint chips and suspended solids from rinse waters or stripping bath wastes in order to reuse them or extend their life.

8. DISCUSSION AND SUMMARY OF ALTERNATIVES

The various treatment technologies presented in the literature review of this section must be closely examined for their applicability to USAF phenolic wastes. As stated previously, there are two distinctly different phenolic waste streams in the Air Force which require treatment. One consists of the industrial or sanitary wastewater stream with flows ranging from several thousand to several million gallons per day, and phenol concentrations ranging from nondetectable to several hundred mg/l. The other is the highly concentrated (20 to 30 percent phenol) wastes generated at an approximate rate of 50 to 100 gallons per day. In addition, the option also exists to treat a phenolic wastewater at its source. The best example of this is the treatment of paint stripping wastewater at the paint stripping facility. The optimum treatment scheme will thus depend upon the type of wastewater treated.

The following is a summary and discussion of the treatment techniques examined in this section with emphasis on their applicability to Air Force phenolic wastewater.

Granular Activated Carbon (GAC) - GAC treatment has been shown to be effective in removing phenols from Air Force paint stripping wastewater and phenolic industrial wastewaters. Some of the methylene chloride present in the stripper evaporated in the stripping process, and thus, did not significantly increase the organic loading on the carbon. Some of the hexavalent chromium was adsorbed but this did not affect the thermal regenerability of the carbon. A minimum contact time of 30 minutes should be used to effectively treat the phenolic paint stripping wastewater. Suspended solids concentration in the influent to a downflow column should be less than 60 mg/l, and the oil content should be less than 20 mg/l. It appears that GAC can be used to effectively treat either the phenols in the paint stripping waste or the industrial waste stream. The main disadvantage to GAC is the high initial capital cost and the high energy consumption during thermal regeneration of the carbon.

Ozone - Based on the literature review, it is concluded that at least 5 moles ozone/mole phenol (2.5 gms O_3 /gm phenol) should be used to treat phenol wastes. If it is found that the intermediate products at this point are harmful to the environment or subsequent treatment processes, then the ozone dosage should be increased. Ozone treatment could be used on the paint stripping wastewater or as a unit process in the IWTP, but would require a pH adjustment to almost 12 prior to oxidation. Another drawback is that ozone generation requires large amounts of energy.

Hydrogen Peroxide - Hydrogen peroxide has potential for use at the paint stripping operation (to reduce the phenol level leaving the facility), IWTP as a polishing step, and possibly in the batch treatment of the highly concentrated phenol wastes. The H_2O_2 :phenol weight ratio should be 20:1 (or more) in conjunction with a ferrous sulfate catalyst. The pH of the wastewater should be adjusted to 3 to 4 during chemical oxidation.

Potassium Permanganate - Based upon the literature findings, potassium permanganate may have potential in treating phenol at the source and will be further investigated for this use. The wastewater pH should be between 7 and 10, and a KMnO_4 :phenol weight ratio of 30:1 is recommended. The use of KMnO_4 for batch treatment of high level phenol wastes, and for IWTP effluent polishing is not considered feasible due to the MnO_2 sludge problem.

Iron (VI) Ferrate - There was only one reference in the literature pertaining to the oxidation of phenol by iron (VI) ferrate. It is apparently still in the experimental stage and has not been tested or used on an actual waste. Because this compound has not been shown to be effective in treating an actual phenolic waste stream it will not be further investigated.

Catalytic Oxidation - One report described and evaluated an aqueous phase catalytic oxidation process designed for 99 percent removal of phenol from two wastewater streams. However, various technical problems remain to be solved if this process is to be applied commercially; thus this technique will not be further addressed in this report.

Chlorine - Chlorine can combine with phenols to produce chlorophenols which are even more toxic and refractory than phenols. Therefore, chlorination is not considered to be an appropriate technique for phenol oxidation and is ruled out as a possible alternative.

Chlorine Dioxide - Unlike chlorine, ClO_2 does not produce chlorophenols, but attacks the benzene ring of the phenol to form compounds that are odorless and tasteless. In the pH range of 7.0 to 8.0, ClO_2 will oxidize the phenol compounds to benzoquinone with a theoretical requirement of 1.5 times the amount of phenol. Chlorine dioxide could possibly be used for treating

the phenolic paint stripping waste at the source or as a unit process in the IWTP. A ClO_2 :phenol weight ratio of 3:1 is recommended in treating these wastewaters.

Aeration (Non biological) - Field tests have shown that some phenol removal can be obtained by aeration alone, either quiescent or forced. However, nonbiological aeration would not be nearly as effective as biological aeration (e.g., aerated lagoon or activated sludge) and is therefore not considered a feasible approach.

Recovery Systems - Recovery systems would have potential in treating the highly concentrated phenol wastes and possibly the paint stripping waste. The waste should be solids-free and pH-adjusted prior to the recovery process. However, it is not known to what extent other contaminants from the waste (e.g., methylene chloride, dichlorobenzene, surfactants and oil and grease) will interfere with the solvent extraction process. If recovery is/becomes a cost-effective treatment method, then a laboratory study should be undertaken to investigate its technical feasibility on these wastes.

Thermal Processes - Both incineration and pyrolysis may be feasible for the disposal of highly concentrated phenolic wastes. However, pyrolysis requires further research for its applicability to these wastes, and thus, only incineration is considered viable at this time. Incineration of hazardous wastes is expected to become more costly following promulgation of RCRA.

Landfill Disposal - The fate of phenol in soil environments is difficult to predict at present. There is little information in the scientific literature concerning the behavior of phenol in soils, its possible reactions, and its alteration by soil components. Landfill disposal might be appropriate for the highly concentrated phenol waste (in drums) if regulatory approval is granted under the rules of RCRA.

Biological Treatment - Activated sludge would be the most effective biological unit process in the IWTP for phenol removal. In addition, an aerated trickling filter or a rotating biological contactor could have potential in treating the paint stripping wastes.

Source Control - Although source control is not actually a treatment technique, it can aid in phenolic pollution abatement. Some examples of source control include: (a) the development of a paint system not requiring phenolic strippers, (b) the development of an effective non-phenolic stripper, (c) removal of concentrated paint stripping wastes from the paint strip facility floor prior to wash-down of the aircraft surface, (d) removal of stripper and old paint with squeegees or industrial vacuum cleaners, (e) filtration of suspended solids from the paint stripping baths in order to reuse or extend the life of these baths. These source control measures should be further studied and implemented if feasible and cost-effective. However, source control is not a treatment or disposal method and its feasibility and cost are not investigated in this report.

Table 9 gives a summary of the feasible alternatives which are further screened in the next section from an economic standpoint.

TABLE 9. SUMMARY OF FEASIBLE TREATMENT TECHNIQUES
FOR USAF PHENOLIC WASTEWATERS

<u>Treatment Technique</u>	<u>Potential Application(s)</u>		
	<u>Aircraft Paint Stripping Waste</u>	<u>IWTP Unit Process</u>	<u>Highly Concentrated Stripping-Bath Wastes</u>
Granular			
Activated Carbon	X	X	
Ozone	X	X	
Hydrogen			
Peroxide	X	X	X
Potassium			
Permanganate	X		
Chlorine			
Dioxide	X	X	
Recovery			
Systems	X		X
Incineration			X
Landfill			
Disposal			X
Biological			
Treatment	X	X	

SECTION III

COST ANALYSES OF FEASIBLE TREATMENT ALTERNATIVES

1. DISCUSSION

The 1979 present value costs of the treatment techniques listed in Table 9 are determined in this section. An attempt is made to compute the cost appropriate to the specific application. For example, a biological treatment unit applied to the paint stripping waste would clearly have a different cost than the same used to treat the entire industrial waste stream for phenols. This approach will enable a comparison to be made, not only among various alternatives within each of the wastewater categories, but between treating the waste at the source versus "the end of the pipe."

In order to make a valid comparison of the alternative processes within each wastewater category, it is necessary that the process meet an arbitrary effluent standard. For treatment of the "aircraft paint stripping wastewater" an average phenol effluent standard of 10 mg/l is imposed, which represents an average removal efficiency of 99.6 percent. In evaluating the unit process for its potential in treating the "industrial waste stream," an average phenol effluent standard of 0.1 mg/l* is imposed, which represents 99 percent phenol removal. Lastly, it is assumed that the technique for treating/disposing of the "highly concentrated stripping-bath wastes" must recover/destroy/dispose of at least 99 percent of the phenol. The recovered phenol has a sales value and will thus contribute a negative cost (i.e., a credit) to the recovery system.

* This phenol standard is quite representative of those presently being imposed upon industrial discharges by the states/EPA.

The economic analysis is performed over an arbitrary 10-year period, and the discount rate is assumed to be 10 percent. Annual operation and maintenance (O&M) costs are transformed to present value costs by multiplying them by the present worth factor corresponding to the 10-percent compound interest rate - 6.144. The resulting value is then added to the capital cost to determine the project's total present value cost (TPVC). This TPVC, which incorporates the capital and O&M costs, forms the basis for economic comparison among alternatives. The Chemical Engineering (CE) Plant cost index, Marshall and Swift (M&S) Equipment cost index, and other miscellaneous cost indices are used to adjust past cost data to the present year (1979). Differential inflation is assumed to be negligible. All equipment/systems are assumed to have a 10-year economic life.

The approach described above will allow an equitable cost-effective analysis for comparing and screening the alternatives. In many instances however, the available cost data from various sources are scanty or entirely lacking. For these cases the costs are estimated from best available information and engineering judgment. Based upon the cost study which follows, the most promising (i.e., cost-effective) alternatives are selected for treatment of Air Force phenolic wastewaters.

2. COSTS OF ALTERNATIVES FOR TREATING AIRCRAFT PAINT STRIPPING WASTEWATER

From the literature survey of the previous section it is concluded that the following techniques are feasible for the treatment of aircraft paint stripping waste:

- Granular Activated Carbon (GAC)
- Ozone
- Hydrogen Peroxide

- Potassium Permanganate
- Chlorine Dioxide
- Recovery Systems
- Biological Treatment

The waste flow is assumed to be 10 gpm and to have the characteristics shown in Table 1. It is assumed that the system operates 250 days/year and must reduce the phenol concentration to an average of 10 mg/l.

a. GAC Treatment of Aircraft Paint Stripping Wastewater

Costs for a GAC treatment system were estimated by Perotti (Reference 4) in 1975. Using the "Equipment, Machinery, and Supports" component index of the CE Plant cost index, these 1975 capital costs were multiplied by $266.5/194.7 = 1.37$ to adjust them to 1979. These adjusted costs are shown in Table 10. Similarly, the 1975 estimated operating costs were updated to 1979 utilizing an average of the M&S Electrical and Steam Power indices for updating energy; the Department of Commerce Hourly Earnings index for updating maintenance and operating labor; and a 1979 cost for GAC of 60¢/lb.

Over an arbitrary economic analysis period of 10 years and a discount rate of 10 percent, this O&M cost translates to a present value cost (PVC) of \$600,000*. Therefore, the total present value cost (TPVC) for this system is \$430,000 plus \$600,000 or \$1,030,000.

* This figure is obtained by multiplying the annual O&M costs (which constitute a uniform series of payments) by the present worth factor, 6.144.

TABLE 10. MAJOR CAPITAL AND O&M COST ESTIMATES (1979)
FOR 10 GALLONS PER MINUTE CARBON TREATMENT SYSTEM OF
AIRCRAFT PAINT STRIPPING WASTEWATER

Capital Investment

Equalization tank (8 hours capacity)	
Contact column (200 ft ³ carbon)	
Carbon storage tanks (spent and regenerated at 3-day supply)	
Miscellaneous, including pumps, piping, instruments, etc.....	\$192,000
Regeneration furnace, including dewatering screen, quench tank, afterburner, controls, etc.....	\$233,000
Activated carbon inventory for initial column charge and 3-day supply at \$0.60/lb.....	<u>\$ 5,200</u>
Total installed costs.....	\$430,000

Annual Operation and Maintenance

Energy (natural gas, electricity, steam).....	\$ 17,500
Maintenance (including carbon regenera- tion and related activities) and operating labor.....	\$ 58,300
Carbon make-up at 0.60/lb (based on 5% regeneration losses).....	<u>\$ 21,800</u>
Estimated total annual operating and maintenance costs.....	\$ 97,600

b. Ozone Treatment of Aircraft Paint Stripping Wastewater

It is assumed that 5 moles of ozone per mole of phenol (equivalent to 2.55 grams O_3 /gram phenol) are required to reduce the paint stripping waste phenol concentration to a 10 mg/l average. (This assumption is in accordance with experimental results achieved by Kroop (Reference 9) and Eisenhauer (Reference 10).) Assuming that the average phenol concentration in the paint stripping waste is 2600 mg/l with a wastewater flow rate of 10 gpm, the ozonator would need an output of 790 pounds O_3 /day. Gumerman, et al., (Reference 45) estimated the cost of this size ozonator as \$880,000 (August 1978). Using the Equipment, Machinery and Supports cost index, this is adjusted to a 1979 cost of \$970,000. In addition, a 45 cubic-foot (ft^3) contact chamber estimated to cost \$10,000 is needed to provide a 30-minute detention time. Typical air-fed ozonation units usually produce up to about 100 pounds O_3 /day. Thus, the ozonator for this waste would require supplemental oxygen. The total annual operating cost was also estimated by Gumerman, et al., to be \$80,000/year in 1978. This is adjusted to 1979 using the M&S Electrical Power cost index yielding \$89,000. However, this does not include the cost of sodium hydroxide addition, necessary to raise the pH (to about 11.5) for effective phenol oxidation. This is estimated to cost about \$5,000/year. This increases the total O&M cost to \$94,000 per year. This annual cost yields an equivalent PVC for O&M of \$580,000. Therefore, the TPVC for the 10-gpm ozone treatment system comes to \$1,560,000. These costs are summarized in Table 11.

TABLE 11. ESTIMATED 1979 COST FOR OZONE TREATMENT OF
AIRCRAFT PAINT STRIPPING WASTEWATER

Capital Investment

Ozone generator (790 lb/day).....	\$970,000
Contact chamber (45 ft ³).....	\$ <u>10,000</u>
Total capital.....	\$980,000

Annual Operation and Maintenance

Electrical energy, oxygen, labor and maintenance.....	\$ 89,000
Sodium hydroxide.....	\$ <u>5,000</u>
Total O&M.....	\$ 94,000

c. Hydrogen Peroxide Treatment of Aircraft Paint Stripping Wastewater

It is assumed (based on the literature review) that an H₂O₂: phenol:iron weight ratio of 2000:100:1 is required to yield an average effluent phenol concentration of 10 mg/l. Thus, the paint stripping wastewater (with an average phenol concentration of 2600 mg/l) must be treated with 52,000 mg/l H₂O₂ and 26 mg/l of iron catalyst. At a flow rate of 10 gpm (14,400 gpd) this amounts to 2,834,000 grams (6240 pounds) of H₂O₂ and 1420 grams (3.12 pounds) of iron per day. The iron catalyst is normally obtained in the form of ferrous sulfate (FeSO₄). Therefore, 8.5 pounds of FeSO₄ are required to yield 3.12 pounds of Fe²⁺ in solution. In addition, about 40 pounds of H₂SO₄/day are required to reduce the pH for optimum phenol oxidation.

The 1979 bulk costs for H_2O_2 , FeSO_4 , and H_2SO_4 are 46.5¢/lb*, 3.3¢/lb, and 2.9¢/lb, respectively. Therefore, the operating cost for chemicals is \$724,000 annually, being primarily controlled by H_2O_2 usage. A chemical feed system is estimated to cost \$60,000 (Reference 45). A 45-ft^{3**} mixing basin (which includes mixer, motor and drive, accessories, handling and setting, piping, concrete, instrumentation, electrical, paint and indirect costs) has a 1972 installed cost of \$28,000 according to Blecker and Nichols (Reference 46). The 1979 capital cost for the basin is computed to be \$55,000 by using the Equipment Machinery and Supports cost index. Assuming a wage of \$8/hr and 2500 hrs/yr (with 0.3 man/yr) the O&M cost (excluding chemicals) is calculated to be \$6700. Thus, the total O&M cost is about \$736,000 and the TPVC is \$4,640,000. These costs are summarized in Table 12.

d. Potassium Permanganate Treatment of Aircraft Paint Stripping Wastewater

It is assumed that a KMnO_4 :phenol weight ratio of 30:1 is required to oxidize the wastewater to an effluent phenol concentration of 10 mg/l. Potassium permanganate effectively oxidizes phenol in the pH range from 7 to 10. Thus, no pH adjustment is required for this process. At a price of 68¢ per pound for KMnO_4 , its yearly cost comes to \$1,600,000. A 9,400 lb/day KMnO_4 feed system would cost approximately \$80,000, and a 45-ft³ mixing basin comes to \$55,000. Maintenance and labor come to \$7,000 and \$6,000 per year, respectively. Hence, the total O&M cost is about \$1,613,000 and the TPVC is \$10,000,000. These costs are summarized in Table 13.

* Based on 32.5¢/lb for 70 percent solution of H_2O_2 .

** This volume provides a 30-minute contact time at 10 gpm.

TABLE 12. ESTIMATED 1979 COST FOR H₂O₂ TREATMENT OF
AIRCRAFT PAINT STRIPPING WASTEWATER

Capital Investment

Mixing basin (45 ft ³).....	\$ 55,000
Chemical feed system.....	\$ <u>60,000</u>
Total capital.....	\$115,000

Annual Operation and Maintenance

Chemicals (H ₂ O ₂ , FeSO ₄ , H ₂ SO ₄).....	\$724,000
Labor (0.3 man/yr, 2500 hr/yr at \$8/hr).....	\$ 6,000
Maintenance (at 5% of capital cost).....	\$ <u>6,000</u>
Total O&M.....	\$736,000

TABLE 13. ESTIMATED 1979 COST FOR KMnO₄ TREATMENT OF
AIRCRAFT PAINT STRIPPING WASTEWATER

Capital Investment

Chemical feed system.....	\$ 80,000
Mixing basin (45 ft ³).....	\$ <u>55,000</u>
Total capital.....	\$135,000

Annual Operation and Maintenance

Chemical (KMnO ₄ at 67¢/lb).....	\$1,600,000
Labor (0.3 man/yr, 2500 hr/yr, at \$8/hr).....	\$ 6,000
Maintenance (at 5% of capital cost).....	\$ <u>7,000</u>
Total O&M.....	\$1,613,000

e. Chlorine Dioxide Treatment of Aircraft Paint Stripping Wastewater

Commercial generation of chlorine dioxide has been accomplished in the past by means of the reaction between chlorine and sodium chlorite in acid solution. The approximate cost (January 1976) of chlorine dioxide is given by Culp, et al., (Reference 47) as \$1.67/pound*. This is adjusted to 1979 using the Wholesale Industrial Chemicals index which yields a 1979 cost of \$2.23/pound. It is assumed that 3 pounds of ClO_2 are required to oxidize 1 pound of phenol. Thus, the annual cost for ClO_2 is calculated to be \$525,000. The costs for chlorine feed systems have been estimated by Patterson and Banker (Reference 48) of Black and Veatch, Consulting Engineers. For a system generating 936 pounds/day of ClO_2 the 1971 capital cost was \$65,000 which includes chlorine feeding and handling equipment, scales, evaporators, structures housing the equipment, and chlorine storage space. Using the CE Equipment Machinery and Supports cost index, the 1979 cost for this system is determined to be \$132,000. A 45-ft³ contact chamber is estimated to cost \$10,000, and would provide 30 minutes detention time. The cost for utilities, manpower, and maintenance are estimated at \$20,000 per year. Therefore, the total annual O&M cost and capital investment for this system are \$545,000 and \$142,000, respectively, yielding a TPVC of \$3,490,000. These costs are summarized in Table 14.

* Based on sodium chlorite at \$1.20/pound and chlorine at \$0.11/pound.

TABLE 14. ESTIMATED 1979 COST FOR ClO_2 TREATMENT
OF AIRCRAFT PAINT STRIPPING WASTEWATER

Capital Investment

Chlorine feed system.....	\$132,000
Contact chamber (45 ft ³).....	\$ <u>10,000</u>
Total capital.....	\$142,000

Annual Operations and Maintenance

Chemical (ClO_2 at \$2.23/lb).....	\$525,000
Labor, maintenance and utilities.....	\$ <u>20,000</u>
Total O&M.....	\$545,000

f. Phenol Recovery of Aircraft Paint Stripping Wastewater

Cost estimates for various phenol recovery systems were given by a number of references (14, 27, 28, 29, 31, 52, 53). Based on these estimates the capital and annual O&M costs for a recovery system to treat the 10-gpm waste flow are roughly \$500,000 and \$200,000, respectively. These costs would cover the installation of adsorption, distillation, and separation equipment, resin, engineering, construction supervision, site preparation, solvent losses, utilities, labor and maintenance. The above system should be able to produce an effluent containing under 10 mg/l phenol and a recovered phenol product with a purity of 99 percent. Assuming that this phenol is salable at the current price of 30¢ per pound, the yearly value of the recovered phenol is calculated to be \$23,000. Thus, the net annual O&M cost is \$177,000 and the resulting TPVC for this system is \$1,600,000.

g. Biological Treatment of Aircraft Paint Stripping Wastewater

The capital cost of an aerated trickling filter system which includes meters, valves, equalization tank, storage tank, mixing tank, batch reactor, pump, piping, and nutrient feed assembly is estimated at \$200,000. The annual O&M cost which is primarily governed by energy and manpower requirements is estimated to be \$30,000. This yields a TPVC of \$384,000.

3. COSTS OF ALTERNATIVES FOR TREATING PHENOLS AT THE INDUSTRIAL WASTE TREATMENT PLANT (IWTP) OR SEWAGE TREATMENT PLANT (STP)

Based on the literature review, the following processes are considered feasible for the treatment of phenols at the IWTP or STP:

- Granular Activated Carbon
- Ozone
- Hydrogen Peroxide
- Chlorine Dioxide
- Biological Treatment

The waste stream is assumed to be 1 mgd with a phenol concentration of 10 mg/l. The system operates 365 days/year and must yield an effluent phenol concentration of 0.1 mg/l.

a. GAC Treatment at the IWTP or STP

Costs for GAC treatment were extracted from Smith's (Reference 49) article "Cost of Conventional and Advanced Treatment of Wastewater." For a 1-mgd system the 1967 capital cost and O&M cost were \$320,000 and 10¢/1000 gallons, respectively. The capital cost is adjusted to 1979 using the Equipment, Machinery and Supports component of the CE Plant Cost Index. The O&M cost is adjusted by using an average of the Marshall & Swift Electrical Power cost index and the Wholesale Chemical price index. These adjustments yield 1979 capital and O&M costs of \$940,000 and 26¢/1000 gallons (\$95,000/year), respectively. Over an economic life of 10 years and a discount rate of 10 percent, this yields a TPVC of \$1,500,000 for the GAC unit process.

b. Ozone Treatment at the IWTP or STP

A flow of 1 mgd with a phenol concentration of 10 mg/l is assumed. The phenol concentration in the final effluent is required to be 0.1 mg/l, which constitutes a 99-percent removal efficiency. To raise the pH of a 1-mgd flow to over 11, and then neutralize prior to discharge would not be economically feasible. Therefore, it is assumed that a 5:1 ozone to phenol weight ratio will compensate for not adjusting the pH. A 420-pound/day ozone generator would satisfy this requirement and has a 1979 cost of \$650,000 (Reference 45). In addition, a 2800-ft³ contact chamber would be needed to provide a 30-minute detention time. The 1979 cost for the chamber is \$20,000 (Reference 45), which brings the total capital cost to about \$670,000. The O&M cost was also estimated by Gumerman et al., (Reference 45), and, adjusted to 1979, is \$54,000. Thus, the TPVC for this system is estimated to be \$1,000,000.

c. Hydrogen Peroxide Treatment at the IWTP or STP

A weight ratio of 2000:100:1 (H_2O_2 :phenol:iron) is assumed necessary to reduce the effluent phenol concentration from 10 mg/l to 0.1 mg/l. A 1670-pound/day H_2O_2 feed system is estimated to cost \$30,000. The annual cost of chemicals for this system is determined to be \$315,000. A 2800-ft³ contact basin is needed to provide a 30-minute detention time, whose capital cost is calculated to be \$20,000. Therefore, the total capital cost and TPVC for this option are \$50,000 and \$2,000,000, respectively.

d. Chlorine Dioxide Treatment at the IWTP or STP

A feed system which generates about 250 pounds ClO_2 /day is required to provide 99-percent phenol removal of the 10 mg/l phenol from a 1-mgd waste stream. This system is estimated to cost \$72,000 in 1979. In addition, a contact chamber is required which provides at least a 30-minute detention time. The 1979 cost of a 2800-ft³ contact chamber is estimated at \$20,000 and the annual cost of chlorine dioxide is approximately \$204,000. Utilities, operating labor, and maintenance are estimated to cost \$15,000 per year. Thus, the total annual O&M cost is \$219,000 and the capital investment is \$92,000. This yields a TPVC of \$1,440,000.

e. Biological Treatment at the IWTP or STP

According to the literature, a well-operated activated sludge plant should be capable of reducing a 10 mg/l phenol influent down to 0.1 mg/l. The 1977 cost of an activated sludge unit process was reported by EPA (Reference 50) in the form of a regression equation:

$$C = 2.27 \times 10^5 Q^{0.87}$$

where:

C = Capital construction cost (\$)

Q = Average wastewater flow (mgd)

The 1977 cost for a 1-mgd activated sludge process is thus \$227,000. This is adjusted to 1979 using EPA's Small City Conventional Treatment (SCCT) cost index, which yields a 1979 cost of \$282,000. The total O&M cost for an activated sludge unit is also given by EPA (Reference 51) as:

$$TC = 8.25 \times 10^4 Q^{0.96}$$

where:

TC = Total O&M cost (\$/year)

Q = Average daily flow (mgd)

Therefore, the 1977 O&M cost for the 1-mgd unit is \$82,500 per year. Using an average of the M&S Electrical Power cost index and the Wholesale Industrial Chemicals cost index, this translates to a 1979 annual O&M cost of \$101,000. The resulting TPVC is \$903,000.

4. COSTS OF ALTERNATIVES FOR TREATING/DISPOSING OF STRIPPING BATH WASTES

The following processes are considered feasible for the treatment/disposal of the phenolic wastes from the stripping vats:

- Recovery
- Incineration
- Landfilling

The waste is assumed to be generated at 20,000 gallons per year and contains 25 percent (250,000 mg/l) phenol. The system must recover/destroy/dispose of at least 99 percent of the phenol.

a. Phenol Recovery of Stripping Bath Waste

From numerous references (14, 27, 28, 29, 31, 52, 53) containing recovery system cost information, the capital and O&M costs for a system to recover phenol from the stripping bath wastes are estimated to be \$300,000 and \$50,000 per year, respectively. It is assumed that 99 percent of the phenol can be recovered from this process, with a resulting phenol of 99-percent purity. Thus, approximately 42,000 pounds of phenol (at 30¢/pound) could be sold yielding a credit of about \$13,000 per year. The net O&M cost for this system is then \$37,000 per year, and the TPVC comes to \$530,000.

b. Incineration of Stripping Bath Waste

The capital cost for an incinerator to treat a 3-gpm phenolic waste stream was reported by Thermal Research and Engineering Corporation (Reference 54) to be \$127,000 in 1972. Using the CE Equipment, Machinery and Supports cost index, this equates to a 1979 cost of \$250,000. This incinerator would be able to treat one-month's worth (1670 gallons) of stripping bath waste in a single work day (9.3 hours). A 2000-gallon holding tank is required to store the waste (while pending incineration) which would cost \$15,000. Winter (Reference 55) reported the following equation for incinerator operating costs:

$$\theta = \frac{330QB}{8340C} + 0.2 \left[\frac{Q}{\frac{(8.34)(1440)C}{3}} \right]^{0.6} (T_c)$$

where:

- θ = Annual Operating Cost (\$/yr)
- Q = Daily Phenol Rate (lb/day)
- C = Concentration (lb phenol/lb H_2O)
- B = Cost of fuel per 1000 gal water feed (\$)
- T_c = Capital cost

For a typical Air Logistic Center (ALC) stripping bath operation, the above parameters would have the following values:

- Q = 114 lb/day
- C = 0.25
- B = \$41.85/1000 gal water feed
- T_c = \$250,000

These values yield an annual operating cost for this incinerator of \$14,000. Therefore, the TPVC for this incinerator system is \$350,000.

c. Landfill Disposal of Stripping Bath Wastes

The best cost estimation for this technique is the actual cost of landfill disposal currently used by an Air Force base. At one base, stripping bath wastes are presently being packaged in 55-gallon drums and transported under contract to a chemical waste landfill. The cost of this operation for FY79 was about \$6000 for disposal of approximately 12,000 gallons of waste. The annual cost for disposal of 20,000 gallons of waste would thus be about \$10,000.

Assuming that landfill disposal of these wastes will be permitted after RCRA is promulgated, the cost of this disposal will undoubtedly increase dramatically. This is because of the

strict requirements imposed upon landfills used for disposal of hazardous wastes. Many existing landfills will either be forced out of operation or undergo redesign and reconstruction in order to comply with the new standards. The landfill owner/operator will, of course, pass these additional costs along to the disposer.

5. SUMMARY OF COST ANALYSES

Table 15 summarizes the economic data for the various systems in order of their cost-effectiveness. The most cost-effective techniques are:

- Biological (aerated trickling filter) for the aircraft paint stripping wastewater.
- Biological (activated sludge) for the industrial waste stream.
- Landfill disposal for the stripping bath waste.

If landfill disposal for the stripping bath waste is banned or becomes too costly as a result of RCRA, then it appears that incineration would be the most cost-effective of the remaining alternatives.

In order to obtain a rough estimate of system costs for various flow-concentration regimes, a set of equations has been developed. It is assumed (for all systems except ozone, recovery, incineration, and landfilling) that the capital investment varies with the flow rate to the six-tenth power, and the O&M cost is directly proportional to the phenol loading rate (i.e., lbs/day). The annual O&M cost is then multiplied by 6.144 to convert to present value cost (10 years at 10-percent discount rate), then

added to the capital cost to yield the TPVC. For ozone treatment, the capital cost is assumed to vary with the flow and the six-tenth power of the phenol loading rate. This assumption is made because the cost of ozone generators is based upon their ozone output in pounds per day. (The O&M cost for ozone is, however, derived as explained previously.) For recovery and incineration, the capital cost term of the equation is derived as explained previously; however, for incineration the annual O&M cost is assumed to be inversely proportional to the phenol concentration. This is because the primary O&M cost for incineration is energy, and the greater concentration of phenol in the waste, the less auxiliary fuel is needed to sustain combustion. The annual O&M cost for a recovery system is assumed proportional to the 0.5 power of the phenol loading rate. This adjustment is intended to take into account the credit for the sale of recovered phenol. The total O&M cost for landfilling is assumed to be directly proportional to quantity of waste disposed. The equations are shown in Table 16.

Note that for a given process (e.g., H_2O_2), flow, and loading rate, the equations corresponding to the different waste streams yield different TPVC's. This inconsistency is explained by:

- the different sources from which costs were estimated in this report;
- the error in adjusting costs based upon only two variables (flow and loading rate); and
- the inherent difference in certain cost elements associated with each waste stream (e.g., labor).

These equations should be used only to establish relative costs among alternatives and should not be used (or cited) as the precise cost for a particular system.

TABLE 15. SUMMARY OF COSTS FOR ALTERNATIVE PHENOLIC
WASTEWATER TREATMENT SYSTEMS

<u>System/Process</u>	<u>Capital Investment</u>	<u>Annual O&M Cost</u>	<u>Total Present Value Cost(TPVC)</u>
I. AIRCRAFT PAINT STRIPPING WASTEWATER: 10 gpm-2600 mg/l Phenol			
a. Biological	\$200,000	\$ 30,000	\$ 384,000
b. GAC	430,000	97,600	1,030,000
c. Ozone	980,000	94,000	1,560,000
d. Recovery	500,000	177,000	1,600,000
e. Chlorine Dioxide	142,000	545,000	3,490,000
f. Hydrogen Peroxide	115,000	736,000	4,640,000
g. Potassium Permanganate	135,000	1,613,000	10,000,000
II. INDUSTRIAL WASTE STREAM: 1 mgd (694 gpm) - 10 mg/l Phenol			
a. Biological	\$282,000	\$101,000	\$ 903,000
b. Ozone	670,000	54,000	1,000,000
c. Chlorine Dioxide	92,000	219,000	1,440,000
d. GAC	940,000	95,000	1,500,000
e. Hydrogen Peroxide	50,000	315,000	2,000,000
III. STRIPPING BATH WASTE: 20,000 gal/yr (0.04 gpm) - 250,000 mg/l			
a. Landfill	\$ 0	\$10,000	\$ 61,000
b. Incineration	265,000	14,000	350,000
c. Recovery	300,000	37,000	530,000

TABLE 16. EQUATIONS FOR APPROXIMATING SYSTEM COST UNDER
VARIOUS FLOW-CONCENTRATION REGIMES

I. AIRCRAFT PAINT STRIPPING WASTEWATER.

- a. Biological: TPVC = $200,000 (Q_1/10)^{0.6} + 184,000 (P/312)$
- b. GAC: TPVC = $430,000 (Q_1/10)^{0.6} + 600,000 (P/312)$
- c. Ozone: TPVC = $10,000 (Q_1/10)^{0.6} + 970,000 (P/312)^{0.6} + 578,000 (P/312)$
- d. Recovery: TPVC = $500,000 (Q_1/10)^{0.6} + 1,090,000 (P/312)^{0.5}$
- e. ClO_2 : TPVC = $142,000 (Q_1/10)^{0.6} + 3,350,000 (P/312)$
- f. H_2O_2 : TPVC = $115,000 (Q_1/10)^{0.6} + 4,500,000 (P/312)$
- g. $KMnO_4$: TPVC = $135,000 (Q_1/10)^{0.6} + 9,910,000 (P/312)$

II. INDUSTRIAL WASTE STREAM.

- a. Biological: TPVC = $282,000 Q_2^{0.6} + 621,000 (P/83.4)$
- b. Ozone: TPVC = $20,000 Q_2^{0.6} + 650,000 (P/83.4)^{0.6} + 332,000 (P/83.4)$
- c. ClO_2 : TPVC = $92,000 Q_2^{0.6} + 1,350,000 (P/83.4)$
- d. GAC: TPVC = $940,000 Q_2^{0.6} + 584,000 (P/83.4)$
- e. H_2O_2 : TPVC = $50,000 Q_2^{0.6} + 1,940,000 (P/83.4)$

III. STRIPPING BATH WASTE.

- a. Landfill: TPVC = $61,000 Q_3$
- b. Incineration: TPVC = $265,000 (Q_3/20,000)^{0.6} + 86,000 (25/C)$
- c. Recovery: TPVC = $300,000 (Q_3/20,000)^{0.6} + 227,000 (X/5,000)^{0.5}$

Q_1 = Waste flow in gpm

Q_2 = Waste flow in mgd

Q_3 = Waste flow in gal/yr

P = Phenol loading rate in lbs/day

X = Phenol loading rate in gal/yr

C = Phenol concentration in percent

SECTION IV

FINDINGS, CONCLUSIONS AND RECOMMENDATIONS

1. FINDINGS AND CONCLUSIONS

- Biological processes are by far the most cost-effective alternative for the treatment of aircraft paint stripping wastewater. The system considered was an aerated trickling filter, which has been shown (in laboratory studies) to effectively treat this type of waste.
- For treatment of phenols in the industrial/sanitary waste stream, the activated sludge process is most cost-effective, closely followed by ozone systems. However, the difference in Total Present Value Cost (TPVC) between activated sludge and ozone treatment is small enough that the cumulative errors inherent in cost estimation could make these two alternatives roughly comparable in cost-effectiveness.
- The most cost-effective method for treatment of the concentrated stripping bath wastes is (presently) disposal in a chemical waste landfill. However, due to stringent regulations being imposed upon such landfills as a result of the Resource Conservation and Recovery Act (RCRA), this method may become either a lot more costly or banned entirely. If the future economics or legality of the situation dictate, incineration of these wastes would be the next best alternative. The economics of a phenol recovery system make it unfavorable at this time.
- A set of equations has been developed to estimate the TPVC of a system/process under various flows and phenol concentrations. These equations are useful for establishing the relative costs among alternatives for flow-concentration regimes different from those assumed in this report.

2. RECOMMENDATIONS

- For an Air Force base having a distinct, major source of phenolic wastewater (e.g., the paint stripping and carbon removal facilities) which requires treatment, a biological system (e.g., aerated trickling filter or a rotating biological contactor) should be employed at the source.

- An Air Force base with only minor sources of phenolic wastewater requiring treatment should employ an activated sludge system at the industrial/sanitary waste treatment plant to reduce the phenol level. However, the difference in TPVC between activated sludge and ozone treatment is small enough that the cumulative errors inherent in cost estimation could make these two alternatives roughly comparable in cost-effectiveness. In fact, according to equations developed in this report, if the phenol loading in the waste stream is under about 35 pounds/day at 1 mgd, then ozone treatment becomes more cost-effective than biological. Therefore, a more detailed cost analysis tailored to the unique circumstances at the base (where a phenol waste treatment system is required at the IWTP or STP) should be performed which compares these two alternatives.

- The highly concentrated phenolic wastes (e.g., from carbon removal and paint stripping baths) should be disposed of in a hazardous waste landfill in accordance with the applicable state/EPA hazardous waste regulations. If the cost of this method becomes more than incineration (or if landfill disposal of this waste is prohibited), a switch to incineration should be initiated.

- Research and development work in the area of biological treatment of phenols should continue in order to develop even more efficient and effective systems/processes. Research should also be conducted in the use of pyrolysis for treating the highly concentrated phenolic wastes.

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